THE ANODIC OXIDATION OF ALUMINUM IN LIQUID AMMONIA

by

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B.S., Sterling College, 1947

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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January, 1951

ACKNOWLEDGMENT

I wish to express my great indebtedness to Dr. A. W. Davidson and Dr. Jacob Kleinberg for their enthusiasm, guidance, and willing help. I further wish to express my gratitude to the Research Corporation for a Frederick Gardner Cottrell grant which has made this work possible.

W. E. B.

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INTRODUCTION

In accordance with Faraday's law, the number of gram-equivalents of a substance that is deposited upon or dissolved from either electrode in an electrolyic process is defined exactly by the quantity of electricity utilized in the process. In many electrolytic processes, apparent deviations from this law occur. An outstanding example of such deviation is encountered in the study of the anodic corrosion of aluminum.

Del Boca (1) reported, in 1933, that he had found the anodic dissolution of aluminum to occur with an abnormally high current efficiency. In a single reported experiment with a cupric nitrate electrolyte it was found that only about 0.5 faraday of electricity was required to dissolve one equivalent of aluminum, if it was assumed that only the tripositive ion of the element was formed.

Del Boca did not regard his results as constituting evidence that aluminum enters the solution with a charge of one. He believed that either the anode aluminum, in part, enters the solution in the form of metal atoms, or that ions such as $(Al^{III}_{3} \cdot Al^{0}_{2})^{+++}$ are formed. Makishima (2), in a general study of the electrolytic properties of liquid ammonia, presented the hypothesis that, in general, lower valent states are more stable with respect to higher valent states in this solvent than in water. He cited the above findings of del Boca as exemplification of this, and suggested that unipositive

aluminum may have been formed.

Booth and Merlub Sobel (3) reported on anodic corrosion current efficiencies for the electrolysis of aluminum iodide in liquid ammonia with an aluminum anode. They found that from 0.96 to 1.36 faradays of electricity was required for the dissolution of one-third gram-atomic weight of aluminum; i.e. of one gram equivalent on the basis of the exclusive formation of the tripositive ion.

Brown, Holmes and King (4) found, with a solution of ammonium azide in liquid ammonia as electrolyte, that from 1.13 to 1.32 faradays of electricity was required to dissolve at the anode one equivalent of tripositive aluminum. Small amounts of nitrogen were observed to be evolved at the anode.

Wöhler and Buff (5), in the electrolysis of aqueous sodium chloride solutions, noted current efficiencies of 125% for the anodic corrosion of aluminum. Turrentine (6), in similar studies, reported hydrogen evolution at the aluminum anode. Turrentine reported a time lag in the evolution of the anodic hydrogen, which indicated that the lower valent aluminum formed was not immediately oxidized. We have carried out an experiment in a divided cell with an aqueous solution of sodium chloride and an aluminum anode. An anodic current efficiency of 115% was obtained. The rate of hydrogen evolution from the anode compartment was found to be that expected on the basis of the reduction of water by all lower valent aluminum formed and no lag in the evolution of the hydrogen was noted.

Sborgi and Marchetti (7), in the electrolysis of acetone solutions of lithium chloride, observed abnormally high current efficiencies at an aluminum anode.

Davidson and Jirik (8), in the electrolysis of anhydrous acetic acid solutions of ammonium and sodium acetates with aluminum anodes, observed high current efficiencies which were reported in the form of initial mean valence numbers of aluminum. With an ammonium acetate electrolyte, initial mean valence numbers as low as 2.36 for the anodic dissolution of aluminum were observed. Current efficiencies with sodium acetate as electrolyte corresponded to initial mean valence numbers as low as 2.28. The solutions resulting from these electrolyses showed some slight reducing power toward iodine. The amount of reducing power, however, was always less than that to be expected if the aluminum had remained in the initial lower valence state. Hydrogen was evolved from the sintered glass disk which separated the anode and cathode compartments, but never in amount quite sufficient to account for the loss of reducing power, if it was assumed that this gas resulted from a reduction of the acetic acid by lower valent aluminum.

Mazzitelli (9), in unpublished work in this laboratory, investigated further the anodic corrosion of aluminum in acetic acid, and was able to obtain current efficiencies which corresponded to mean valence numbers as low as 1.80.

Compounds containing aluminum in other than the tripositive state have not been prepared at ordinary temperatures.

At elevated temperatures, unipositive compounds of the element have been produced. For example, Klemm, Geiersberger, Schaeler and Mindt (10) have reported the production of Al_2S and Al_2Se at 1100° to 1200°, and Klemm, Voss and Geiersberger (11) produced aluminum halides of the form AlX at 800° to 1200°.

The purpose of the present work was to attempt to determine the most favorable conditions for high current efficiencies in the electrolytic oxidation of aluminum, and to characterize the processes taking place under these conditions. Liquid ammonia was chosen as a solvent particularly because of its stability towards reduction. Because of this property it was hoped that the aluminum might remain in its lower valent form in the solution. It is a somewhat unfortunate circumstance that, in the work to be described, high current efficiencies were observed only when electrolytes with readily reducible anions were used.

Another reason for the choice of liquid ammonia was that the lowest initial valence numbers found to date were observed when that solvent was used.

EXPERIMENTAL

Materials and Apparatus

The aluminum was obtained from The Aluminum Company of America in the form of rods 0.25" in diameter, the following analysis was reported for it:

Si----------	0.0016%
Fe----------	0.0006%
Cu----------	0.0004% or less
Mg----------	0.0009%
Na----------	0.0006% or less
Ca----------	not detected
Mn----------	not detected

The electrolytes were C.p. products which were carefully freed of water, either by drying or by the formation of ammoniates.

The ammonia was obtained in the anhydrous form and usually received no further treatment.

The nitrogen used to provide an inert atmosphere was dried by being passed successively through drying towers containing sodium hydroxide, calcium chloride, and magnesium perchlorate. For a few of the experiments, traces of oxygen were removed by passing the gas through a heated tube containing copper turnings.

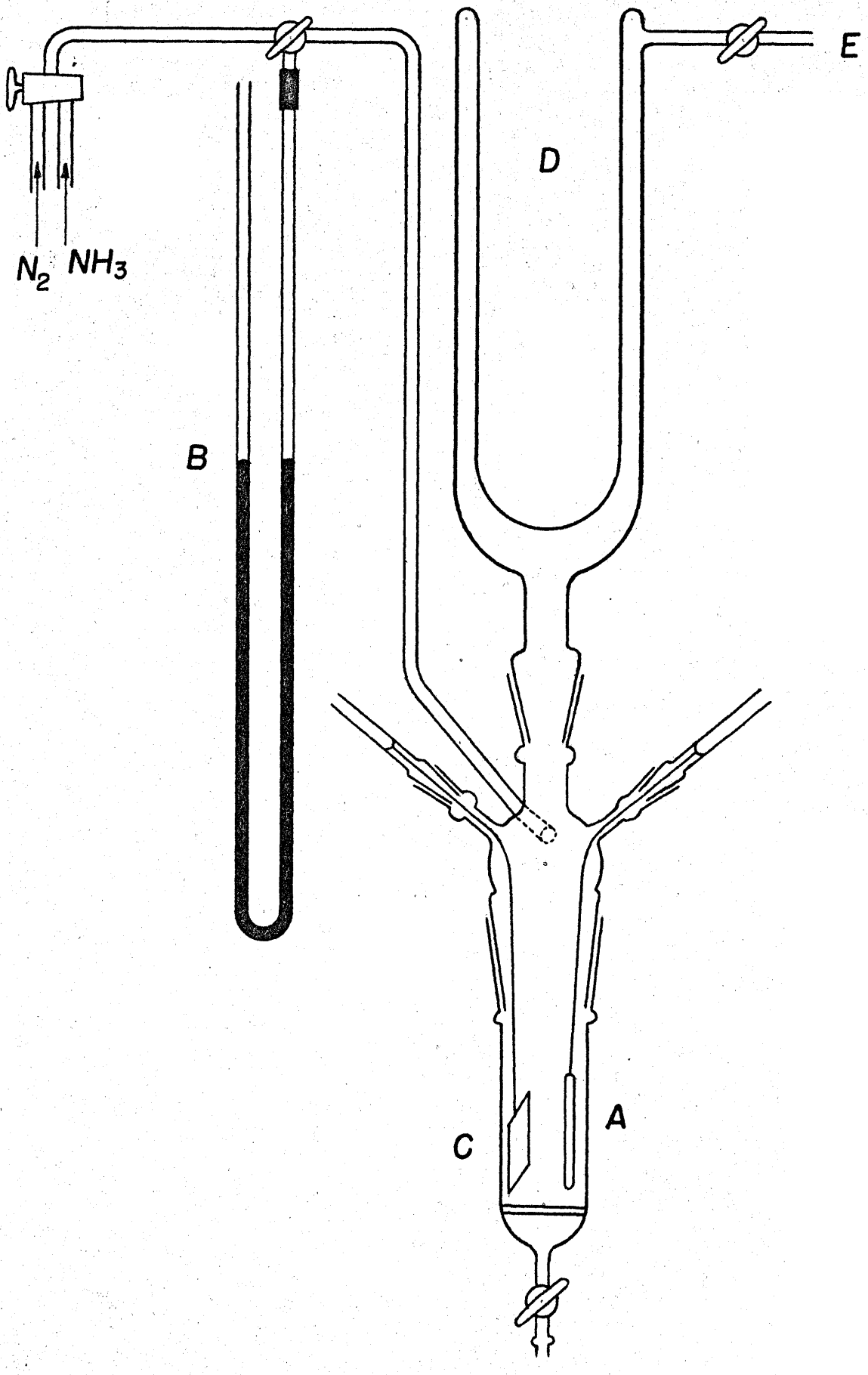
The quantity of electricity passed through the circuit was determined by means of a silver coulometer in series with the electrolysis cell. This coulometer consisted of a silver rod anode and a platinum dish cathode. In the dish,

in contact with the anode, was placed a 5% aqueous solution of silver nitrate. The amount of silver deposited was determined by weighing the washed and dried platinum dish before and after each electrolysis. It was also necessary to filter the silver nitrate solution through a weighed Gooch filter after each electrolysis, since there was a tendency for some silver to become detached from the platinum dish and to be washed out with the solution. It was also necessary to wrap the silver anode with filter paper to collect a small quantity of unidentified black material which fell from the anode during the passage of current through the coulometer.

The source of the direct current was a full-wave rectifier, the voltage output of which could be controlled by a potential divider located at the alternating current input. This rectifier was unfiltered, and would deliver from 0 to 750 volts.

Several different types of electrolysis cells were used. These are pictured in Figures I, II, VII and VIII. The simple cell of Fig. I, in the bottom of which was a sintered glass disk for the purpose of filtering out solid products obtained during the experiment, was connected with an ammonia condenser in which was placed the cooling mixture. (The cooling mixture used in all of the work consisted of powdered Dry Ice and isopropyl alcohol.) With this arrangement the ammonia in the cell was allowed to boil and recondense from

Fig. I



the condenser. This process served the dual purpose of temperature control and stirring action.

The compartments of the divided cells were, in all cases, separated by sintered glass disks. Disks of medium porosity were found to be most satisfactory.

Procedure

The aluminum to be used as an anode was cleaned with concentrated sodium hydroxide solution, rinsed with distilled water, and dried quickly in an oven before being weighed. After the electrolysis the anode was cleaned with distilled water, dried in the oven, and then weighed.

The electrolytes were weighed and placed in the thoroughly dried electrolysis cell; dried nitrogen was then passed through the system for a sufficient amount of time to remove all oxygen and traces of moisture.

The cell was placed in a cooling bath for the condensation of the ammonia. After a suitable amount of ammonia had condensed, the electrolyte was caused to dissolve either by boiling the ammonia or by the use of a magnetic stirrer.

When constant temperatures below the boiling point of ammonia were desired, manual temperature control was used. With efficient stirring, it was not difficult to maintain temperatures constant to within a degree in the range from -70° to -78° by the manual addition of Dry Ice to the cooling mixture.

The measurement of the amount of gas evolved was carried out, in general, as follows. The cooling bath of the cell was brought to some definite temperature where it was maintained for sufficient time to allow the amount of ammonia vapor in the gas to reach equilibrium. The pressure in the cell and in the mercury burette used to collect the gas was made equal to the atmospheric pressure. After the electrolysis, the system was equilibrated to atmospheric pressure, and the temperature of the cell was brought to the same point as before. The gas in the burette was washed with slightly acidulated water, to remove traces of ammonia vapor, before measurement of the amount of gas evolved. The amount of acid in the wash water was sufficiently small so that no change in the vapor pressure of the water occurred. Some variations in the method of measuring the amount of gas evolved will be discussed later.

The amount of hydrogen contained in the gases was determined from the volume change upon combustion of the gas, when ignited by a heated platinum filament, in air or oxygen.

From the loss in weight of the anode, together with the coulometric data, the apparent initial valence number with which the aluminum entered the solution was calculated. This calculation was carried out in the following manner:

w(Al)--loss in weight of the aluminum anode.
N(Al)--number of moles of aluminum dissolved from the anode.

(1) $w(Al)/26.97 = N(Al)$

w(Ag)---weight of silver deposited in the coulometer.
Q----number of faradays of electricity passed.

(2) $w(Ag)/107.88 = Q$

V_I------apparent initial valence number.

(3) $Q/N(Al) = V_I$

Combining (1), (2) and (3):

$$\frac{w(Ag)x26.97}{w(Al)x107,88} = \frac{\text{moles of Ag}}{\text{moles of Al}} = V_I$$

If the aluminum went into solution as the tripositive ion the following would be true:

$3xN(Al) = Q$

However, if the aluminum goes into the solution with a charge of less than three:

$3xN(Al) > Q$

And $3xN(Al)-Q$ = the number of equivalents of reducing power to be expected of the solution due to the anode reaction.

Anodic Oxidation of Zinc

Zinc would be expected to form only the bipositive ion when it is anodically dissolved. For this reason it was thought that a determination of the apparent initial valence number for the dissolution of a zinc anode would serve as a check of the experimental procedure.

Zinc nitrate was used as the electrolyte. It was made anhydrous in the following manner. Ammonia gas was bubbled through a saturated solution of hydrated zinc nitrate in

water until the precipitate which at first formed had redissolved. The solution was cooled and treated with ethanol, which brought about precipitation of the white crystalline zinc nitrate ammoniate. This precipitate was dried at a temperature of 100° C. in an ammonia atmosphere. The product, upon analysis, proved to be $Zn(NO_3)_2 4(NH_3)$.

The simple cell of Fig. I was used. Following is a description of a typical experiment of this type. The cathode was platinum, the anode zinc, and the electrolyte a solution of 1.7 grams of zinc nitrate in 60 cc. of liquid ammonia.

About 2 volts were required to sustain a current of 0.07 amperes. There was deposition of zinc upon the cathode, and no apparent gas evolution or coloration at either electrode. There was no insoluble substance formed. The data and results were as follows:

Electrolysis time--3 hours
Area of anode------6 cm.^{2}
Temperature-------- -33° C.
Silver deposited
in coulometer---0.7944 g.
Current----------0.07 amp.
Weight loss of anode--0.2443 g.
No. of faradays-------0.007364
Apparent initial valence number of zinc----------1.97

Following is a tabulation of the results obtained in this and further experiments. The temperature, area of anode and time of electrolysis were the same throughout the series.

Concentration of electrolyte	Current density	Apparent initial valence number
g./liter	amp./cm.^{2}	
23	0.02	1.95
28	0.01	1.97
32	0.025	1.97
13	0.025	1.96

The fact that the results for the apparent initial valence number were lower than the expected value of 2 by from 1.5% to 2.5% suggests that some non-electrolytic corrosion may have occurred. To test for this a bar of zinc weighing 15 grams was allowed to stand in a boiling liquid ammonia solution of zinc nitrate for three hours, and was found to decrease in weight by 0.0003 grams. This loss of weight is evidence of a slight amount of non-electrolytic corrosion; however, it amounts to only about one-fiftieth of the loss to account for the lower apparent initial valence numbers obtained.

Del Boca carried out similar experiments with zinc at lower temperatures and with electrolysis of long duration. He obtained results which correspond to apparent initial valence numbers of 1.92 and 1.90, and observed a one-milligram loss in weight of a piece of zinc in a saturated solution of zinc nitrate in ammonia for a period of 24 hours.

Since we were concerned with the behavior of aluminum, no further experiments were carried out with zinc.

Anodic Oxidation of Aluminum

Zinc Nitrate Electrolyte--A series of electrolysis were carried out in the simple cell of Fig. 1, with aluminum anodes and zinc nitrate as electrolyte.

The aluminum anodes were made of commercial sheet aluminum, probably not of a high degree of purity. Following is a table of data and results:

Concentration of electrolyte	Electrolysis time	Current density	Apparent initial valence number
g./liter	hours	amp./cm.^{2}	
6.7	2 1/2	0.01	2.83
17	3	0.01	2.66

The anode in these experiments became coated with a deposit, probably of aluminum oxide, which could not be completely removed without danger of removing aluminum also. Consequently the results obtained may be expected to be high.

It is obvious that the apparent initial valence numbers are definitely less than three.

Cupric Nitrate Electrolyte--The anode, in these experiments, was made of the high purity aluminum described in the section on materials. The cupric nitrate, in the form of the ammoniate, was prepared in the same manner as described for the preparation of the zinc nitrate ammoniate. The experiments were carried out in the simple cell of Fig. I at -33°C. The volume of ammonia used was about 60cc. in all cases.

Following is a description of a typical electrolysis. A solution of 0.7 gram of cupric nitrate was used as the electrolyte. Initially 14 volts were required to sustain a current of 0.2 ampere, but the resistance of the cell increased slowly during the run. Copper was deposited on the cathode, and the blue color of the cupric ion gradually disappeared. A white deposit formed, apparently upon the anode. A summary of the data and results follows:

Electrolysis time--3 1/4 hrs. Current----------0.2 amp.
Area of anode------10 cm.^{2} Weight loss of anode--0.1763 g.
Temperature-------- -33° C. No. of faradays-------0.01663
Weight of silver
in coulometer---1.7917 g.
Apparent initial valence number of aluminum----------2.68

Small amounts of aluminum deposit adhere to the anode and could not be completely removed without risk of removal of aluminum from the surface. The amount of deposit remaining in most cases did not amount to more than a few milligrams.

A compilation of the results of several experiments is given below.

Concentration of electrolyte	Electrolysis time	Current density	Apparent initial valence number
g./liter	hours	amp./cm.^{2}	
12	3 1/4	0.001	2.73
12	3 1/4	0.02	2.68
12	1 1/2	0.03	2.61
13	1 1/4	0.02	2.76

A similar listing of the data and results obtained by del Boca is as follows:

Concentration of electrolyte--unknown
Electrolysis time----------12 hours
Anodic current density--------0.0003 to 0.003 amp./cm.^{2}
Apparent initial valence
number----1.48

The results which we obtained do not agree even approximately with that obtained by del Boca. Since del Boca did not go into much detail concerning the purity of his electrolyte and aluminum anode, or the concentration which he used in the single experiment reported the reason for this difference is unknown.

Our results, which are fairly consistent, show a definite decrement in apparent initial valence number, as compared to the theoretical value of three.

Aluminum Nitrate Electrolyte--Aluminum nitrate was made anhydrous by repeatedly washing the salt with liquid ammonia in the electrolysis cell. Ammonia was then condensed upon the portion which had not dissolved. Following is a summary of the data and the results:

Electrolysis time--3/4 hour
Area of anode------10 cm.^{2}
Temperature-------- -33° C.
Weight of silver
in coulometer---0.8481 g.
Current----------0.3 amp.
Weight loss of anode--0.0775 g.
No. of faradays-------0.00785
Conc. of $Al(NO_3)_3$-----17 g./liter
Apparent initial valence number of aluminum----------2.73

A blue color, which disappeared when the current was shut off, was noted at the surface of the cathode.

The result in this case agrees well with those obtained with zinc nitrate and copper nitrate as electrolytes.

Ammonium Nitrate Electrolyte--Ammonium nitrate was dried in an oven at a temperature of about 120° C. This electrolysis was carried out in the large divided cell shown in Fig. II. Following is a summary of the data and results:

Current density------0.01 amp./cm.^{2}
Conc. of electrolyte--45 g./liter
Temperature---------- -78° C.
Weight loss of anode--0.2453 g.
No. of faradays-------0.002460
Apparent initial valence number----------2.71

In this case a white precipitate formed in the anode compartment, while at the cathode gas was evolved. It is to be expected that hydrogen would be evolved at the cathode.

The apparent initial valence numbers obtained with various nitrates as electrolytes consistently have values in the neighborhood of 2.7. There appears to be little, if any, dependence of the apparent initial valence number upon the nature of the cation, whether it be Zn^{++}, Cu^{++}, Al^{+++} or NH^{+}_4. Evidently, then, the cation plays no part in the determination of the current efficiency.

Aluminum Triiodide Electrolyte--Anhydrous aluminum triiodide was prepared by direct reaction between an excess of finely divided aluminum and iodine in a closed tube. This product was distilled into a glass tube, from which a sample of the electrolyte could be taken by breaking off the proper length of the filled tubing. About one gram of aluminum triiodide was dissolved in 60 cc of ammonia in the simple cell of Fig. I.

When the electrolysis was commenced, the first visible result was the formation of a blue coloration near the surface of the cathode. The blue color gradually became more stable, until finally the whole volume of the solution was colored. A large amount of precipitate was formed during the experiment.

The blue solution obtained in this experiment resembled very much the well known alkali metal solutions in this solvent, and it was concluded that the best explanation for it was that a solution of aluminum in liquid ammonia had been formed. The cathode reaction, in such a case, would be the introduction of electrons into the solution to form an "ammoniated electron solution".

When the blue color extends throughout the solution, a probable competing anode reaction would consist of the removal of electrons from the solution. If this occurs to any great extent the apparent initial valence number found in these experiments would be expected to be high. Following are the results obtained in two of these electrolyses:

Concentration of AlI_3	Electrolysis time	Current density	Apparent initial valence number
g./liter	hours	amp./cm.^{2}	
17	3 1/2	0.02	3.08
25	3	0.02	3.05

The apparent initial valence numbers obtained here are quite near to, but slightly greater than, three. It is believed

that, since the concentration of dissolved aluminum was probably quite small, and since only a part of the electrolysis was carried out after the solution was completely colored, only a small increase of apparent initial valence number would result from the competing reaction. It appears that the aluminum goes into solution almost completely in the tripositive form.

The phenomenon of the formation of the blue aluminum solution was reported in the literature (12). Mr. A. D. McElroy, of this laboratory, continued the investigation of this blue solution and obtained further evidence that the interpretation in terms of electron dissolution at the cathode is correct (13).

Cupric Bromide Electrolyte--Cupric bromide was dried in an oven at 100° C. and then kept overnight in a vacuum desiccator. With this electrolyte, electrolyses were carried out in the simple cell of Fig. I at the boiling temperature of the solution. Copper was deposited at the cathode and a white substance was formed at the anode. The solution was slowly decolorized, and the resistance of the cell increased to a small extent. The anode became slightly discolored with a black to brown stain.

Following is a tabulation of data and results:

Concentration of $CuBr_2$	Electrolysis time	Current density	Apparent initial valence number
g./liter	hours	amp./cm.^{2}	
8	2 1/2	0.01	2.96
8	3	0.02	2.97
8	2 3/4	0.02	3.00
15	2	0.03	3.03
15	2	0.03	2.96
15	2	0.03	3.07
15	1	0.04	2.95
		MEAN----------	2.99

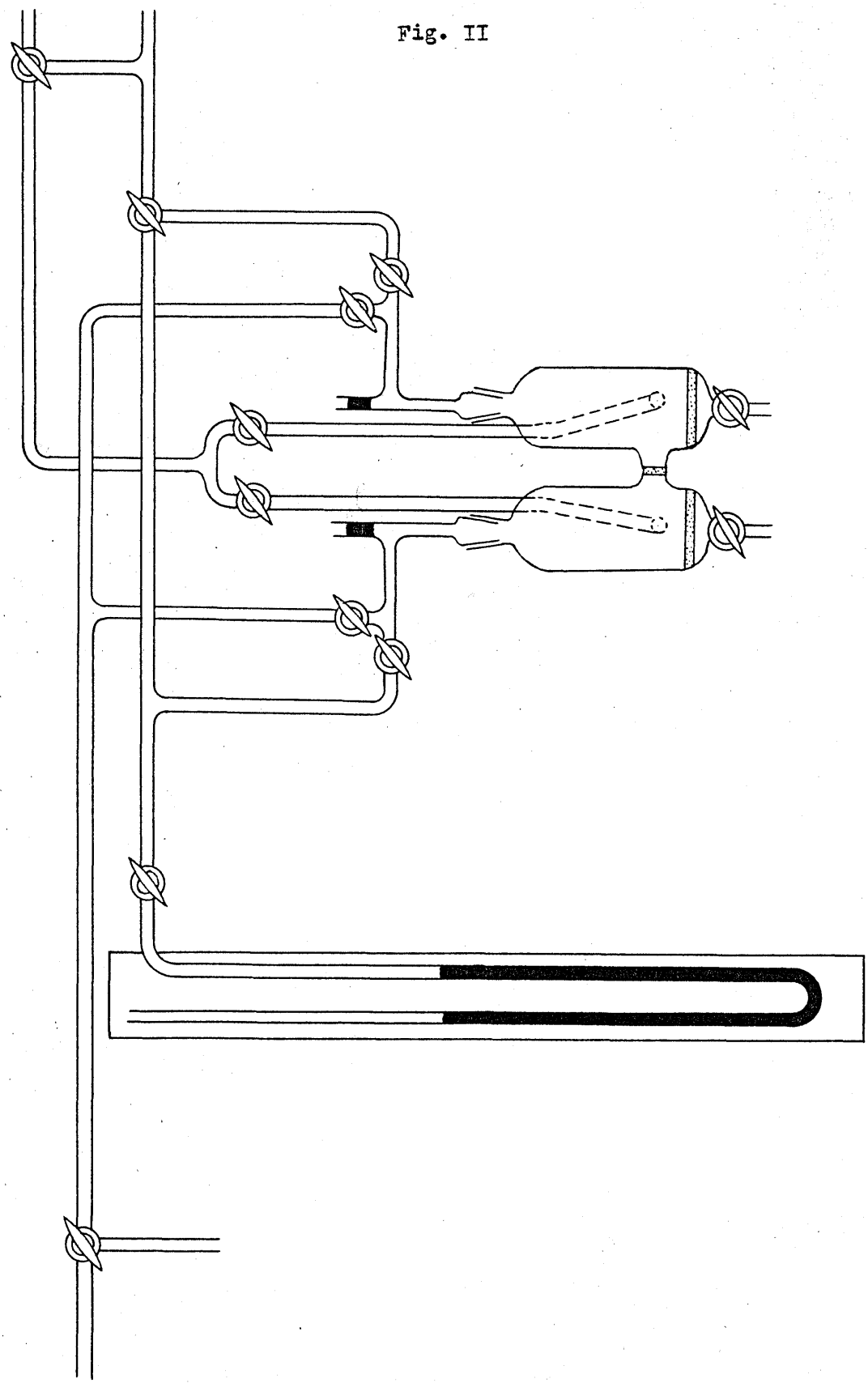
The average of the results lies very near to the value which would be expected if the aluminum entered the solution only in the tripositive state. The average deviation of the results from the mean value of 2.99 was 0.04. This deviation of 1.3% is greater than the expected error in the determination of the apparent initial valence number. Possibly there may be competing reactions taking place at the anode which cause the small variation in the results.

Ammonium Bromide Electrolyte--Pure ammonium bromide was dried in an oven at 120° C. The large divided cell of Fig. II was used, with about 180 cc. of ammonia as solvent.

Gas was evolved at the cathode, and a white precipitate was formed in the anode compartment. The data and results follow:

Conc. of electrolyte--40 g./liter
Temperature-----78° C.
Current density----------0.01 amp./cm.^{2}
Weight loss of anode--0.2463 g.
No. of faradays-------0.00268
Apparent initial valence number----------2.94

Fig. II



This result is near to but slightly less than three. The difference of 0.06 valence unit is somewhat greater than the expected experimental error.

Sodium Thiocyanate Electrolyte--The sodium thiocyanate was dried in an oven at 120° C. The simple cell of Fig. I was used.

The only significant qualtitative observation was that a yellow coloration appeared at both the anode and the cathode. At a low current density, the blue sodium solution did not persist at the cathode. Following are the data and results:

Conc. of electrolyte--25 g./liter
Temperature----- -33° C.
Current density--0.01-0.02 amp./cm.^{2}
Weight loss of anode---0.0680 g.
No. of faradays---0.007465
Apparent initial mean valence number------2.96

This result is comparable to those obtained with halides as electrolyte.

Sodium Cyanide Electrolyte--When an oven dried sample of sodium cyanide was used as an electrolyte in the simple cell of Fig. I the anode became passive; hence apparent initial valence numbers greater than three were obtained.

Sodium Nitrite Electrolyte--Oven dried sodium nitrite, when used as an electrolyte in the simple cell of Fig. I, caused the anode to become passive. An apparent initial valence

number of 6.28 was obtained. During the run a peculiar sparking was noticed upon the surface of the anode, and after the electrolysis the anode was found to be deeply pitted. After the first few minutes of electrolysis it was necessary to increase the potential to 300 volts in order to obtain a current.

Potassium Iodate Electrolyte--With potassium iodate as an electrolyte in the simple cell of Fig. I, the following results were obtained: At first the resistance of the cell was very high, 765 volts being required to give a current density of 0.004 amp./cm.^{2} After one hour the resistance began to decrease, and, after about twenty more minutes, only 200 volts were required to maintain a current density of 0.01 amp./cm.^{2} This lowering of resistance may have been due to the formation of potassium iodide as a result of the cathode reaction. Possibly iodite and hypoiodite are formed also. Data and results follow:

Conc. of electrolyte--17 g./liter
Temperature----- -33° C.
Current density---0.004-0.01 amp./cm.^{2}
Weight loss of anode--0.0157 g.
No. of faradays--0.001762
Apparent initial valence number----------3.03

Potassium Permanganate Electrolyte--When this electrolyte was used the anode became decidedly passive, and sparking was noted on its surface. An apparent initial valence number of 11 was obtained.

Ammonium Acetate Electrolyte--Anhydrous ammonium acetate was prepared by placing anhydrous acetic acid in the cell. This reacted with ammonia to give the ammonium salt. The anode became passive, as is indicated by the following results:

Concentration of NH_4OAc	Electrolysis time	Current density	Apparent initial valence number
g./liter	hours	amp./cm.^{2}	
85	3	0.01	3.5
85	1	0.01	3.5

Ammonium Salicylate Electrolyte--Ammonium salicylate was prepared by the direct reaction between salicylic acid and the solvent. The anode became passive, giving a valence of 7.23.

Aluminum Acetylacetonate Electrolyte--This electrolyte was prepared as described in "Inorganic Synthesis", Vol. II (14). The simple cell of Fig. I was used. The current fell off almost to zero after several minutes of electrolysis, probably because of the formation of a viscous film upon the anode. Following are the data and results:

Conc. of electrolyte--17 g./liter
Temperature----- - 33° C.
Current density---0.00-0.01 amp./cm.^{2}
Weight loss of anode--0.0136 g.
No. of faradays--0.00144
Apparent initial valence number----------2.9

Due to the fact that this electrolysis was of comparatively short duration, the accuracy was not great. The result may be regarded as equal to 3, to within the experimental error.

A compilation of all results obtained with the simple electrolytes described up to this point appears in Table I.

Conclusions

Of all the simple electrolytes used, only nitrates gave apparent initial valence numbers appreciably lower than three. Halides, sodium thiocyanate, potassium iodate, and aluminum acetylacetonate gave values near to three. Other anions, such as nitrite, permanganate, acetate, and salicylate caused the aluminum anode to become passive; i.e., reactions other than the dissolution of aluminum took place.

There appears to be no obvious dependence of the apparent initial mean valence number upon the nature of the cation.

Gas Evolution Determination

Cupric nitrate was used as an electrolyte in a small divided cell in order to determine the extent of gas evolution at the anode during the electrolysis.

A relatively large amount of gas evolution from the anode compartment was observed. However, most of the gas appeared to be evolved from the surface of the sintered glass disk which separated the two compartments of the cell. This gas was found to be nitrogen. The portion of the anode gas, which comes from the sintered disk, evidently does not result from an electrolytic process at the anode. It might be supposed that the disk acts as a catalyst for the oxidation of ammonia to nitrogen.

TABLE I

Electrolyte	Concentration	Time	Current density	Apparent initial valence number
	g./liter	hours	amp./cm.^{2}	
$Cu(NO_3)_2$	10	3	0.01	2.71
"	10	3	0.02	2.68
"	10	1 1/2	0.03	2.62
$Zn(NO_3)_2$	7	2 1/2	0.008	2.85
"	17	3	0.01	2.66
$Al(NO_3)_3$	17	1	0.03	2.73
NH_4NO_3	50	1 1/2	0.01	2.71
AlI_3	17	3 1/2	0.02	3.08
"	25	3	0.02	3.05
$CuBr_2$	8	2 1/2	0.01	2.96
"	8	3	0.02	2.97
"	8	2 3/4	0.02	2.99
"	15	2	0.03	3.03
"	15	2	0.03	2.96
"	15	2	0.003	3.07
"	15	1	0.04	2.95
NH_4Br	40	1 1/2	0.01	2.94
Aluminum acetylacetonate	17	few min.	0.0 -0.03	2.9
$NaNO_2$	33	1 1/4	0.02-0.03	6.28
NaSCN	25	2	0.01-0.02	2.97
NaCN	17	1	varied	passive
KIO_3	17	1	varied	3.03
$KMnO_4$	17	few min.	varied	passive
Anmonium salicylate	85	3	0.01	3.5-5.15
Anmonium acetate	51	2	0.01	7.2

To determine whether or not all of the nitrogen was evolved at the disk, the cell was altered so that gas from the disk itself might be collected separately from that given off at the anode. Following are the results:

Concentration of electrolyte------	40 g./liter
Volume of ammonia----------	25 cc.
Loss in weight of anode----------	0.1047 g.
No. of faradays----------	0.01112
Apparent init. val. no. ----------	2.86
Volume of gas at anode----------	6.83 cc. (STP)
Volume of gas at disk----------	20.14 cc. (STP)
Total volume of gas----------	26.97 cc. (STP)

If we suppose that only the nitrogen collected directly from the anode, stems from the electrolytic process and if it is further assumed that both the anodic oxidation of amide to nitrogen and the reduction of nitrate to nitrogen by lower valent aluminum occur, the valence becomes 2.62, which corresponds closely with the lower values of apparent valence found in the simple cell, with this same electrolyte. It was necessary to consider the possibility of the competing anode reaction, i.e. the oxidation of amide ion, in order to account for all of the nitrogen evolved.

The rate of gas evolution, in the above experiment, appeared to increase with the time of electrolysis. If a competing reaction does take place at the anode, then extended electrolysis should give high values for the apparent initial valence number. Two experiments to test this were carried out in the same cell used above. The results were as follows:

Concentration of electrolyte	Electrolysis time	Current density	Quantity of electricity	Apparent initial valence number
g./liter	days	amp./cm.^{2}	faradays	
50	2	0.0004-0.01	0.01460	4.85
50	2	0.0005-0.01	0.01538	3.05

The high results show that some reaction other than the dissolution of aluminum indeed occurs at the anode. The increase with time in the extent to which the competing reaction takes place is apparently related to the depletion of the electrolyte.

An electrolysis was carried out with an ammonium nitrate electrolyte of fairly low concentration, so that a competing reaction might occur at the anode. On the assumption of a competing reaction consisting of the oxidation of amide, and also that the lower valent aluminum reduced nitrate to nitrogen, an apparent valence number of 2.61 was obtained. On the assumption of no competing reaction at the anode an apparent valence number of 3.41 was obtained. It appears that, when nitrates are used as electrolytes, the actual initial valence number is about 2.6; because of the occurence of the competing anode reaction however, many of the results, if calculated only upon the basis of weight loss, come out considerably higher than this.

Anodic Oxidation of Aluminum in Mixed Electrolytes

The marked difference between the behavior of the nitrates and that of the halides suggested the use of mixtures of the two types of salts.

Mixtures of cupric nitrate and bromide as electrolytes were the first to be tried in this portion of the study. The simple cell of Fig. I was used. The volume of ammonia in all cases was about 60 cc. Following is a table of data and results:

Conc. of $Cu(NO_3)_2$	Conc. of $CuBr_2$	Elect. time	Current density	Quant. of elect.	Apparent initial valence number
g./liter	g./liter	hours	amp./cm.^{2}	faradays	
5.0	11.7	3/4	0.03	0.00844	1.80
8.3	8.3	1	0.03	0.01117	1.55
8.3	8.3	1	0.03	0.00917	1.56
12.5	4.2	1	0.03	0.01087	2.19
15	1.7	1	0.03	0.00956	2.62

There emerges from this series of experiments a striking dependence of the apparent initial valence number upon the relative proportions of nitrate and bromide in the electrolyte. The minimum value of 1.55 is much lower than any previously obtained with the use of simple electrolytes.

To determine whether or not there was any non-electrolytic corrosion of the aluminum anode, a piece of aluminum weighing 4.9 grams was immersed in 20 cc. of a

boiling liquid ammonia solution containing 0.2 grams each of copper nitrate and bromide. After exposure of one hour no observable change of weight was found, although a decrease as little as 0.00005 gram could have been detected.

A similar series of determinations was made with sodium nitrate-sodium halide mixtures. The electrolyses were carried out in the simple cell of Fig. I at the boiling temperature of the solution. Some semi-quantitative experiments with sodium nitrate-bromide mixtures gave apparent initial valence numbers as low as 1.85, and some with sodium nitrate-chloride mixtures as low as 1.72 but with sodium nitrate-iodide mixtures, however, no low valences were obtained. The results appeared sufficinetly significant to warrent further investigation, of a much more quantitative nature, of the dependence of the apparent initial valence number upon the relative concentrations of salts in the electrolyte.

First, a series of determinations were carried out with sodium nitrate-sodium bromide mixtures as electrolyte in the simple cell of Fig. I. The volume of ammonia, in all cases, was about 60 cc., and the temperature was the boiling point of the solution.

A source of error in the determination of the ratio of nitrate to bromide lies in the fact that, during condensation of ammonia into the cell, changes of pressure force a little of the solution below the sintered glass disk before

all of the electrolyte has dissolved. This factor, however, is believed to cause an error of no more than one per cent in the mole percentage of bromide in the solute. Since it was difficult to condense an accurately determined amount of liquid ammonia into the cell the total amount of ammonia may vary from 60 cc. by as much as 3 or 4 cc. Such variation, however, would produce very little error in the results, since, provided that the total concentration of electrolyte was relatively large, there was found to be very little dependence of the apparent initial valence number upon the total concentration.

In Table II are listed the data and results of these experiments. A graphical representation of the results appears in Fig. III.

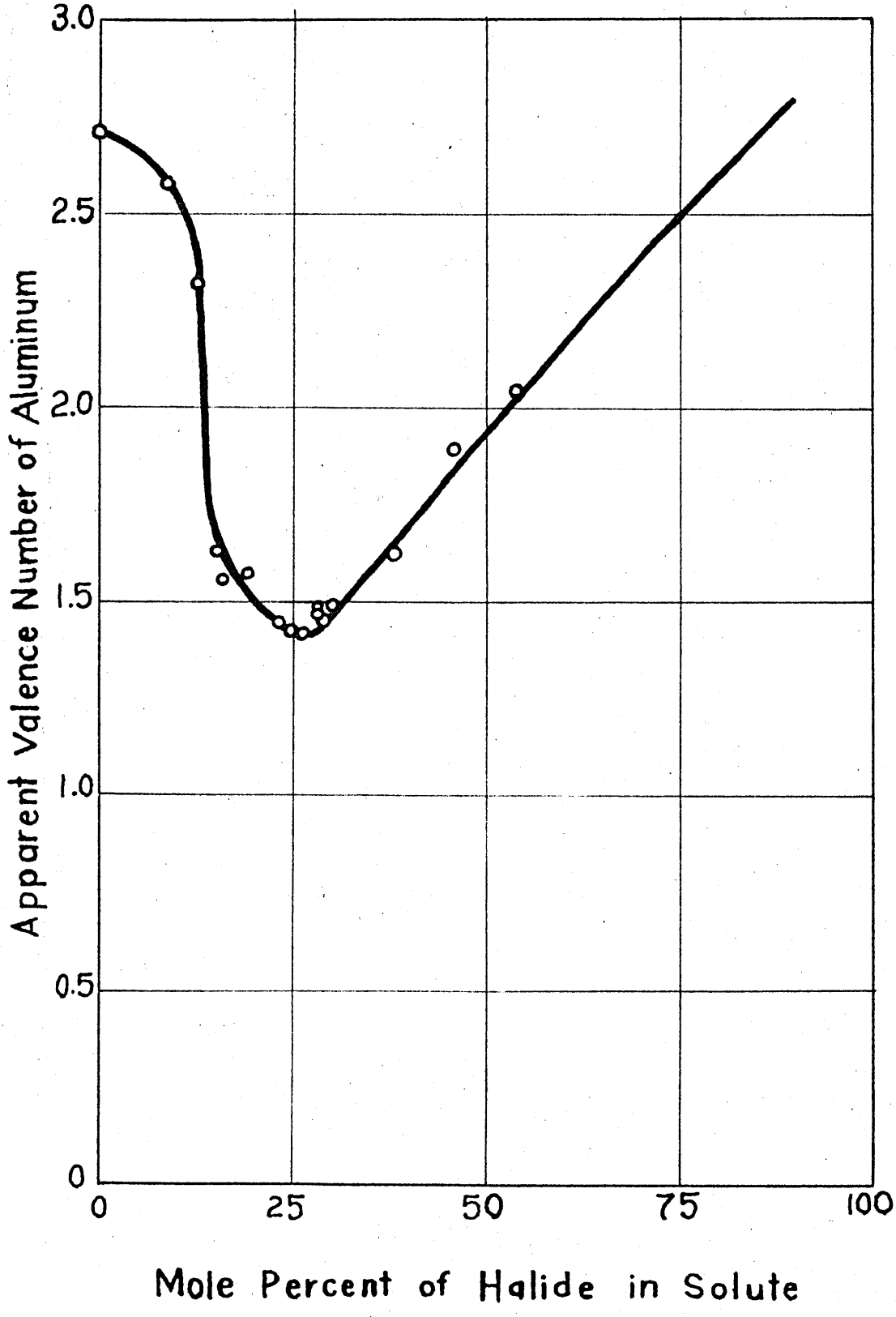
The cathode deposit in each of these experiments was in the form of a dark blue-black tree. When the current was shut off, this deposit gradually turned yellow. The yellow product exploded when brought into contact with moisture. It probably consists of the salt Na_2NO_2, the formation of which in liquid ammonia solutions, was reported by Maxted (15) and by Zintl and Kohn (16). It was prepared by them in two ways; by the electrolysis of sodium nitrite in liquid ammonia, and by the treatment of a solution of sodium nitrate in liquid ammonia with a solution of sodium.

If the liquid ammonia was removed from the cell immediately after the current had been shut off, the dark

TABLE II

Number of moles of $NaNO_3$	Number of moles of NaBr	Mole % NaBr in solute	Elect. time	Current density	Apparent initial valence number
			min.	amp./cm.^{2}	
0.00803	0.00947	54.1	96	0.02	2.04
0.00975	0.00850	46.3	92	0.02	1.89
0.01177	0.00718	38.1	93	0.02	1.62
0.01294	0.00563	30.3	101	0.04	1.49
0.01317	0.00534	28.9	110	0.03	1.45
0.01332	0.00532	28.5	97	0.02	1.48
0.01336	0.00529	28.4	107	0.03	1.47
0.01377	0.00495	26.4	110	0.03	1.42
0.01412	0.00469	25.0	120	0.03	1.43
0.01447	0.00446	23.6	110	0.02	1.45
0.01530	0.00369	19.5	100	0.02	1.57
0.01603	0.00309	16.2	107	0.02	1.56
0.01624	0.00291	15.2	110	0.03	1.63
0.01668	0.00250	13.0	115	0.02	2.32
0.01766	0.00175	9.02	110	0.02	2.58

Figure III


3.0
2.5
2.0
1.5
1.0
0.5
0
Apparent Valence Number of Aluminum
0
25
50
75
100
Mole Percent of Halide in Solute

deposit did not turn completely yellow. The blue color slowly disappeared, and a white powder remained which contained traces of the silvery color of metallic sodium.

Whenever low valences (in the neighborhood of 1.5) were obtained, the anode appeared to be corroded very uniformly. The greater the apparent initial valence number, the greater was the degree of roughness of the electrode surface. In no case, however, was there any evidence of mechanical disintegration of the anode.

An anode deposit was noted in all cases. This deposit was white to light gray in color, and, when low valences were obtained, it did not adhere to the anode. Since the separation of anode and cathode deposits was difficult, chemical tests were not made upon the products.

The resistance of the cell, in all cases, slowly increased during the electrolysis. This increase indicated a change in the concentration or in the nature of the electrolyte, the reasons for which will be discussed later.

During one of the electrolyses a piece of aluminum weighing about 3 grams was immersed in the solution, but left unconnected to either electrode. No change in mass was observed.

The apparent initial valence numbers unmistakably show a regular dependence upon the relative proportions of the two salts in the electrolyte. A minimum of 1.42 was observed when the electrolyte initially consisted of 26.4 mole per cent

of sodium bromide.

A similar series of determinations was made with sodium nitrate-sodium chloride mixtures. Unfortunately sodium chloride is not as soluble as sodium bromide, a concentration of 5 grams per liter being about the highest that could readily be obtained.

The data and results for these experiments appear in Table III. A graphical representation of the results appears in Fig. IV.

The cathode deposits were much like those obtained in the case of the sodium nitrate-sodium bromide mixtures. The anode deposit was white and crystalline in appearance.

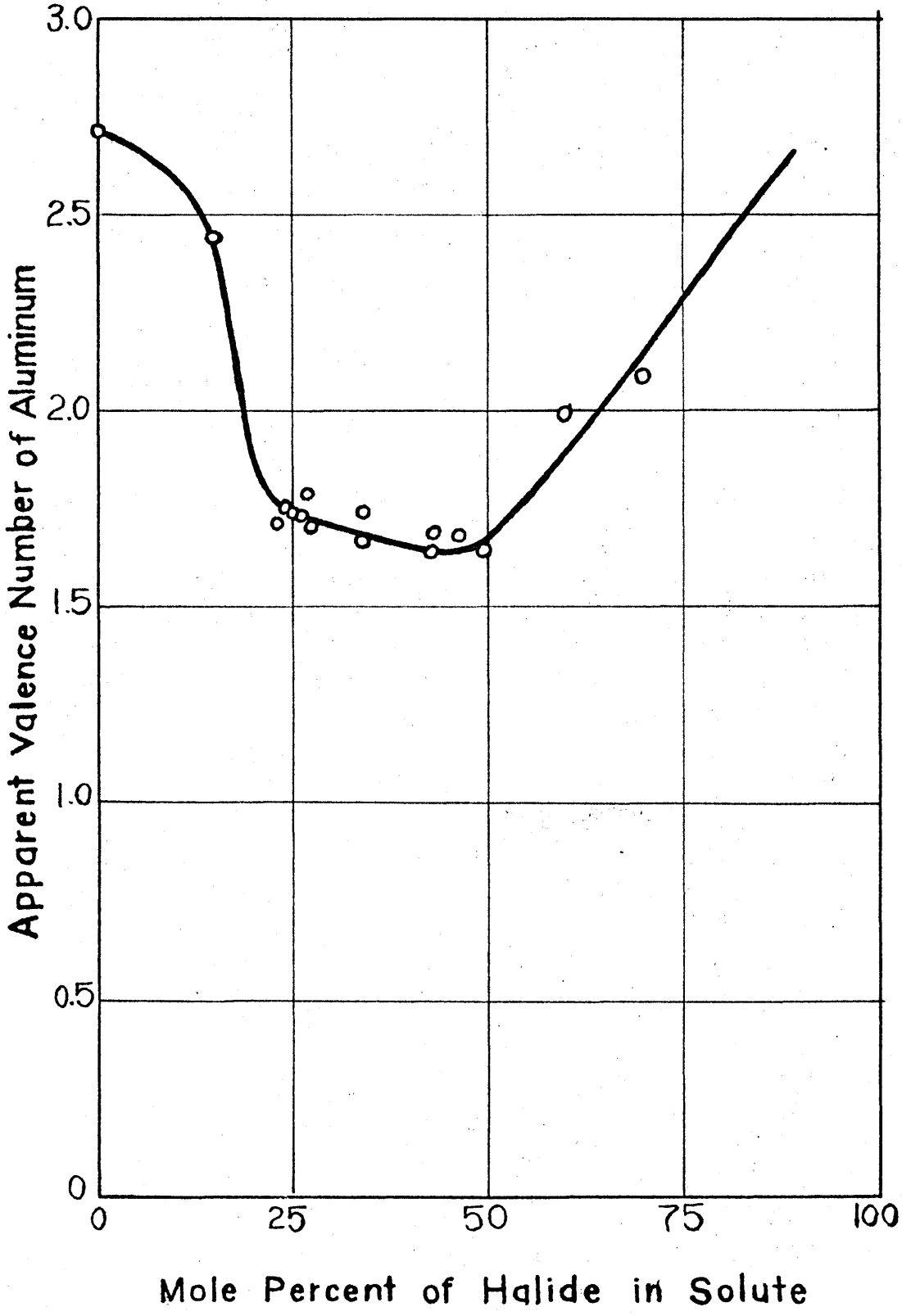
The apparent initial valence numbers pass through a minimum of 1.63, when the mole per cent of sodium chloride in the electrolyte is 42.8. The curve obtained in this case is broader than in the case of the sodium nitrate-sodium bromide mixtures, and does not show so low a minimum.

A secondary cathode reaction consists in the reduction of nitrate, which, of course, brings about a change in the relative concentrations of the electrolytes; during the course of the electrolysis the proportion of sodium bromide would be expected to increase hence the resultant apparent initial valence number is a sort of average value for the range of concentrations traversed. Because of this effect, curves representing the true dependence of the apparent valence upon the proportion of bromide in the solute would

TABLE III

Number of moles of $NaNO_3$	Number of moles of NaCl	Mole % NaCl in solute	Elect. time	Current density	Apparent initial valence number
			min.	amp./cm.^{2}	
0.00758	0.001762	69.9	33	0.01	2.08
0.01180	0.001776	60.1	37	0.01	1.98
0.01770	0.001767	49.7	40	0.01	1.64
0.002027	0.001764	46.6	44	0.01	1.68
0.02364	0.001765	42.8	35	0.01	1.68
0.02355	0.001770	42.8	80	0.02	1.63
0.0341	0.001767	34.2	53	0.02	1.66
0.0682	0.003523	34.0	120	0.02	1.74
0.01093	0.004125	27.6	113	0.02	1.70
0.01126	0.003745	26.7	113	0.02	1.785
0.01588	0.00566	26.3	95	0.02	1.73
0.01607	0.00537	25.0	115	0.04	1.74
0.01623	0.00514	24.0	110	0.02	1.75
0.01141	0.00343	23.1	120	0.02	1.71
0.00998	0.001765	15.0	56	0.02	2.44

Figure IV


3.0
2.5
2.0
1.5
1.0
0.5
0
Apparent Valence Number of Aluminum
0
25
50
75
100
Mole Percent of Halide in Solute

lie somewhat to the right of the experimentally found curves of Figures III and IV. Calculations show that, if the cathode reaction is rapid, the corrected curve in the neighborhood of the minimum would be shifted to the right about 6% in the case of the sodium nitrate-bromide mixtures, and about 7% for the sodium nitrate-chloride mixtures. This correction would also flatten out the curve at the minimum, and corrected, the curve should show a lower minimum apparent initial valence number.

Two other effects may also change the relative concentrations of the components of the mixed electrolyte. The first of these is the formation of the insoluble anode product. If this product contains the electrolyte anions in a ratio different from that in the solution, the concentrations would be altered from the original value. The second possibly is that if the nitrate ion is reduced by lower valent aluminum which is formed, the concentration of nitrate in the electrolyte would decrease.

All of the above effects may be minimized if large amounts of electrolyte are used in proportion to the amounts of products formed. The use of a divided cell would minimize the effect of the cathode reaction.

In the next series of electrolyses, a mixture of sodium nitrate and sodium cyanide was used as electrolyte, in the simple cell of Fig. I. The volume of solvent was 60 cc. The data and results follow:

Number of moles of $NaNO_3$	Number of moles of NaCN	Mole % NaCN in solute	Elect. time	Current density	Apparent initial valence number
			min.	amp./cm.^{2}	
0.00179	0.01400	88.7	40	0.03	3.74
0.01130	0.01210	49.6	30	0.03	2.52
0.00923	0.00513	35.7	60	0.02	2.50
0.01138	0.00402	26.1	60	0.03	2.79

There was a slight lowering of valence number below that found with the pure nitrate as an electrolyte; however, there was also some evidence of a competing reaction taking place at the anode. In all cases there was a visible gas evolution at the anode.

Electrolyses in a Divided Cell

In order that the anode and cathode products might be kept separate, and also to decrease the effect of the cathode reaction upon the relative concentrations of electrolyte in the anode compartment, a series of experiments were undertaken in the large divided cell of Fig. II. The capacity of this cell was 180 cc., and this quantity of liquid ammonia was used in all electrolyses. With this large volume, increased amounts of electrolyte could be used, and hence the percentage changes of concentration of electrolytes in the anode compartment resulting from the formation of the anode product, as well as from secondary or competing anode reactions, were decreased.

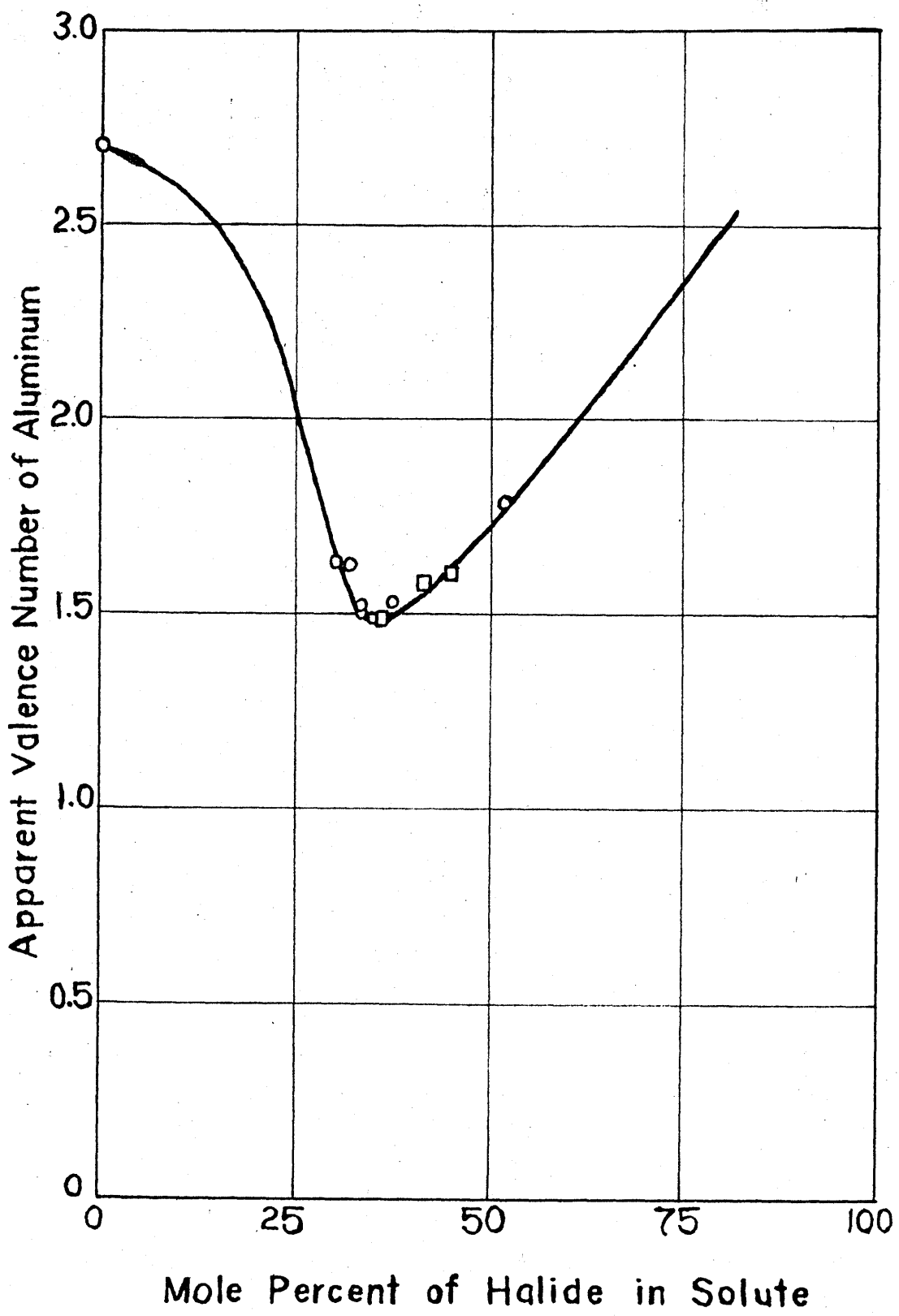
A series of determinations were made of the effect of the relative proportions of sodium nitrate and bromide in the electrolyte upon the mean valence number at a temperature of -78° C. The data and results appear in tabular form in Table IV, and in graphical form in Fig. V. The first eight electrolyses were carried out in a cell similar to that of Fig. II, but having a capacity of 60 cc.; the points, in Fig. V corresponding to these runs are represented by circles. The last three electrolyses were carried out in the larger cell of Fig. II; these points are represented in Fig. V by squares.

From a comparison of Fig. III and V, it may be seen that the curve derived from the divided cell experiments, lies to the right and slightly above that obtained previously from experiments in the simple cell. The shift of the curve to the right was to be expected in consequence of the decrease in the effect of the cathode reaction upon the concentrations of the electrolytes in the neighborhood of the anode. The increase of the minimum from 1.42, in the case of the simple cell, to 1.49, in the case of the divided cell, is somewhat surprising, since a lower minimum valence number was expected. This increase of the minimum apparent initial valence number must be a result of the fact that the divided cell experiments were carried out at -78°, while those in the simple cell were carried out at the boiling temperatures of the solution (about -33°). The attainment of low apparent initial valence

TABLE IV

Number of moles of $NaNO_3$	Number of moles of NaBr	Mole % NaBr in solute	Elect. time	Current density	Apparent initial valence number
			hours	amp./cm.^{2}	
0.006470	0.002815	30.4	3/4	0.02	1.63
0.00636	0.00301	32.2	3/4	0.015-0.02	1.63
0.00646	0.00327	33.6	3/4	0.015-0.02	1.51
0.006380	0.003205	33.5	3/4	0.015-0.02	1.52
0.00630	0.003395	35.1	3/4	0.015-0.02	1.49
0.00624	0.00373	37.4	3/4	0.015-0.02	1.53
0.00588	0.00419	41.6	3/4	0.015-0.02	1.58
0.005305	0.005710	51.8	3/4	0.05	1.78
0.02400	0.01986	45.3	2 3/4	0.007	1.61
0.02367	0.01623	41.4	6 1/2	0.008	1.58
0.02498	0.01400	36.0	5	0.015	1.49

Figure V


3.0
2.5
2.0
1.5
1.0
0.5
0
Apparent Valence Number of Aluminum
0
25
50
75
100
Mole Percent of Halide in Solute

numbers appears to be favored slightly by higher temperatures.

The minimum valence number, in these divided cell experiments, is 1.48, occurring when the electrolyte contains 35.1 mole % of sodium bromide. This corresponds to about one mole of bromide to two of nitrate.

A series of electrolyses were carried out with sodium nitrite-sodium bromide mixtures. The first experiment was carried out in the simple cell of Fig. I at the boiling temperature of the solution, while the remaining four were performed in the large divided cell of Fig. II at a temperature in the neighborhood of -78°. The data and results follow:

Conc. $NaNO_2$	Conc. NaBr	Elect. time	Current density	Apparent initial valence number
g./liter	---	hours	amp./cm.^{2}	
25	25	1 3/4	0.02	2.2
9.96	8.94	4	0.02-0.008	3.6
7.79	12.2	4	0.01	2.8
20	20	10	0.01	2.6
20	20	8	0.01	2.5

In all of these experiments in the divided cell a black deposit was formed in the anode compartment. Some of this material adhered strongly to the anode and could not be completely removed. Because of this fact, the apparent initial valence numbers are only approximate, and may be supposed to be somewhat too high.

This black material reacted with cold water slowly, and with hot water vigorously, with the evolution of hydrogen. This substance appears to be a highly active form of very finely divided metallic aluminum. A sample of the anode product from the second electrolysis was analyzed for aluminum and was found to contain 46% of that element. A sample of the product from the third experiment contained 17.2% of aluminum and 29.9% of bromine. These data demonstrate that the anode product is but a mixture varying in composition from experiment to experiment.

A sample of the black anode product from the fourth experiment was analyzed for free aluminum by treatment with concentrated sodium hydroxide solution in a special cell. The amount of hydrogen evolved and the amount of aluminum in the solution were determined. The sample was found to contain 15% of aluminum, 54% of which was in the metallic state.

There are two possible sources of this highly active metallic aluminum. One possibility is that the anode undergoes mechanical disintegration; the other is that the metal enters the solution as a lower valent ion, which then undergoes disproportionation to the free metal and the tripositive ion. The latter hypothesis appears to be the more plausible.

Because of the fact that when sodium salts were used as electrolytes the cathode reaction interfered by changing the nitrate ion concentration, it seemed desirable to try

some other simple cation which would not cause such complications. Ammonium ion was chosen because the cathode reaction in this case would presumably consist exclusively of the liberation of hydrogen. Furthermore, ammonium salts are, in general, fairly soluble in this solvent. On the other hand, because of its acidity, the use of ammonium ion involved the possibility that the aluminum might be non-electrolytically attacked. Subsequent investigation, however, showed that such attack did not occur.

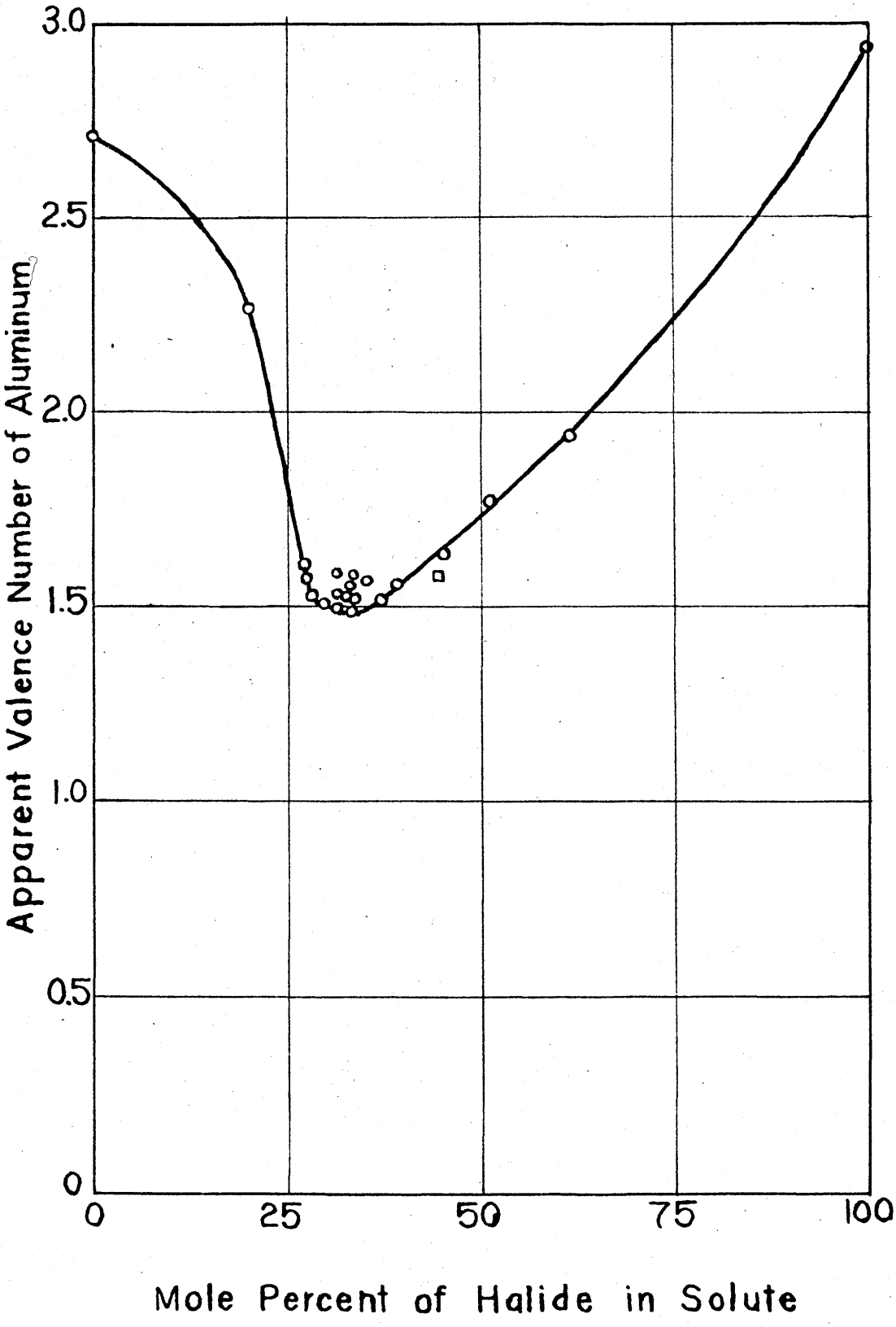
Many electrolyses were carried out, for various purposes, on ammonium nitrate-ammonium bromide mixtures in several different cells. The data for a group of these experiments, selected because the number of faradays of electricity used did not greatly exceed the number of moles of nitrate ion present, appear in Table V and are presented in graphical form in Fig. VI. Because of the large number of determinations made in the neighborhood of the minimum, not all such points are recorded. The data include also a point, indicated by a square, obtained with the use of the corresponding silver salts.

Some of the scattering of the values near the minimum of the curve may be attributed to a change in concentration of one component of the electrolyte, due either to reduction of nitrate or to the precipitation of the anode product. The major source of error in the large divided cell is the entrapment of ammonia below the sintered glass disk before

TABLE V

No.	Number of moles NH_4NO_3	Number of moles NH_4Br	Mole % NH_4Br in solute	Cell type	Current density	App. init. val. no.
				D-divided S-simple	amp./cm.^{2}	
(1)	0.0000	0.0633	100	D-180 cc.	0.01	2.94
(2)	0.02170	0.03595	61.4	"	"	1.94
(3)	0.02855	0.02980	51.2	"	"	1.77
(4)	0.02960	0.02615	45.3	"	"	1.65
(5)	0.03575	0.02283	39.0	"	"	1.56
(6)	0.03630	0.02123	37.0	"	"	1.52
(7)	0.1250	0.06135	33.0	"	"	1.54
(8)	0.1253	0.06170	33.0	"	"	1.56
(9)	0.04080	0.01725	29.7	"	"	1.52
(10)	0.04650	0.01154	19.9	"	"	2.27
(11)	0.1	0.0000	0	"	"	2.71
(12)	0.0606	0.0266	31.6	"	0.015	1.53
(13)	0.0606	0.0266	31.6	"	"	1.59
(14)	0.0651	0.0350	35.0	S-60 cc.	0.02	1.57
(15)	0.0650	0.0360	33.7	"	"	1.59
(16)	0.00675	0.00342	33.6	S-25 cc.	0.01	1.58
(17)	0.06250	0.03073	32.9	"	"	1.49
(18)	0.00793	0.00385	32.7	"	"	1.52
(19)	0.0650	0.03083	32.2	"	0.015	1.55
(20)	0.0654	0.0310	32.2	"	0.01	1.53
(21)	0.0652	0.0308	32.1	"	"	1.50
(22)	0.0650	0.0306	32.1	"	0.015	1.50
(23)	0.0650	0.0306	32.1	"	"	1.50
(24)	0.0672	0.0306	31.3	"	0.001-0.002	1.54
(25)	0.0605	0.0275	31.2	"	0.0005	1.52
(26)	0.01257	0.00532	29.7	S-60 cc.	0.002	1.51
(27)	0.0675	0.0306	28.3	S-25 cc.	0.005	1.53
✓(28)	0.01264	0.00536	33.6	D-60 cc.	0.002	1.52
(29)	0.0375	0.01604	30.0	"	"	1.52
(30)	0.03753	0.01600	29.9	"	0.005	1.51
(31)	0.0325	0.0124	27.6	"	0.002	1.58
(32)	0.0330	0.01235	27.2	"	0.01-0.02	1.61
	$AgNO_3$	AgBr				
(33)	0.00668	0.00535	44.5	S-60 cc.	0.01	1.58

Figure VI


3.0
2.5
2.0
1.5
1.0
0.5
0
Apparent Valence Number of Aluminum
0
25
50
75
100
Mole Percent of Halide in Solute

all of the electrolyte had dissolved. All of the larger known errors in the valence number, in the neighborhood of the minimum, are positive. We therefore feel justified in drawing the curve through the lowest values obtained at that point.

This curve strongly resembles that obtained with the sodium salts in the divided cell, the minimum, however, lies 2 or 3 % to the left of the one shown in Fig. V.

The anode deposits obtained from the electrolysis in the large divided cell appeared upon analysis to be a mixture, the aluminum content ranging from 17 to 24%, and the bromide content being about 10%. This product contained also nitrate ion and a trace of nitrite. Determination of the amount of ammonia evolved upon the treatment of the deposit with sodium hydroxide solution revealed an ammonia content of 23%. The ammonia may have been in the form of NH_3, NH_4^+, NH_2^-, or $NH^=$. The results of later investigations of the anode reaction indicate that some oxide also was probably present.

A quantitative adaptation of a color "spot test" for nitrite was used for the determination of this ion. The process consists essentially of the diazotization of an amine by the nitrous acid, formed by the acidification of the nitrite, with subsequent dye formation.

The solutions used were as follows:

Solution (1) -- 2.5 grams of sulfanilic acid dissolved in 250 cc. of 30% acetic acid.

Solution (2) -- 0.75 gram of napthylamine was placed in 175 cc. of boiling water. The colorless solution was decanted and mixed with 175 cc. of glacial acetic acid.

A measured sample of the aqueous solution to be analyzed for nitrite was placed in a 100 cc. volumetric flask, and 20 cc. of ethyl alcohol was added to prevent the precipitation of the dye which was to be formed; the flask then was filled to the mark with distilled water. One cc. of solution (1) was added and the solution was mixed completely. Then 1 cc. of solution (2) was added, and the flask was shaken until the color, which developes slowly, had reached a constant intensity. The percentage transmission of the solution was determined in a spectrophotometer at the wave length of the absorption peak; 545 millimicrons.

For concentrations of nitrate of the order of 10^{-5} molar, the absorption was found to follow Beer's Law very well. There was found to be no difference in the results whether the diazotization and dye formation were carried out at 0° C. or at room temperature.

Experiment number 5 of Table V was undertaken in order that the products might be analyzed for total nitrite ion. The quantity of electricity used was 0.00488 faraday. The number of equivalents of aluminum present in the solution and products at the end of the experiment was 0.00891. (This figure is based on the assumption that all of the dissolved aluminum eventually was oxidized to the tripositive state.)

The amount of reduction of substances in the solution, as a result of the change in valence of the aluminum from the initial mean valence number to 3, was 0.00891-0.00488 or 0.00403. The spectrophotometric analysis of all products, both those precipitated during the experiment and those left as a residue upon the evaporation of the ammonia, showed only 1.42×10^{-5} mole of nitrite to be present, which corresponds to 2.84×10^{-5} equivalents of reduction of nitrate to nitrite. Even if possible reduction of nitrate to nitrite at the cathode is disregarded, this figure amounts to only 0.7% of the reduction to be expected of the aluminum. Evidently the main reduction product is to be sought elsewhere.

The dissolved and solid products of experiment number 4 of Table V were analyzed for reducing power with iodine as oxidizing agent. No reducing power could be detected by this means. Treatment of part of the anode product resulting from this electrolysis with sodium hydroxide, as a test for free aluminum, resulted in no evolution of free hydrogen.

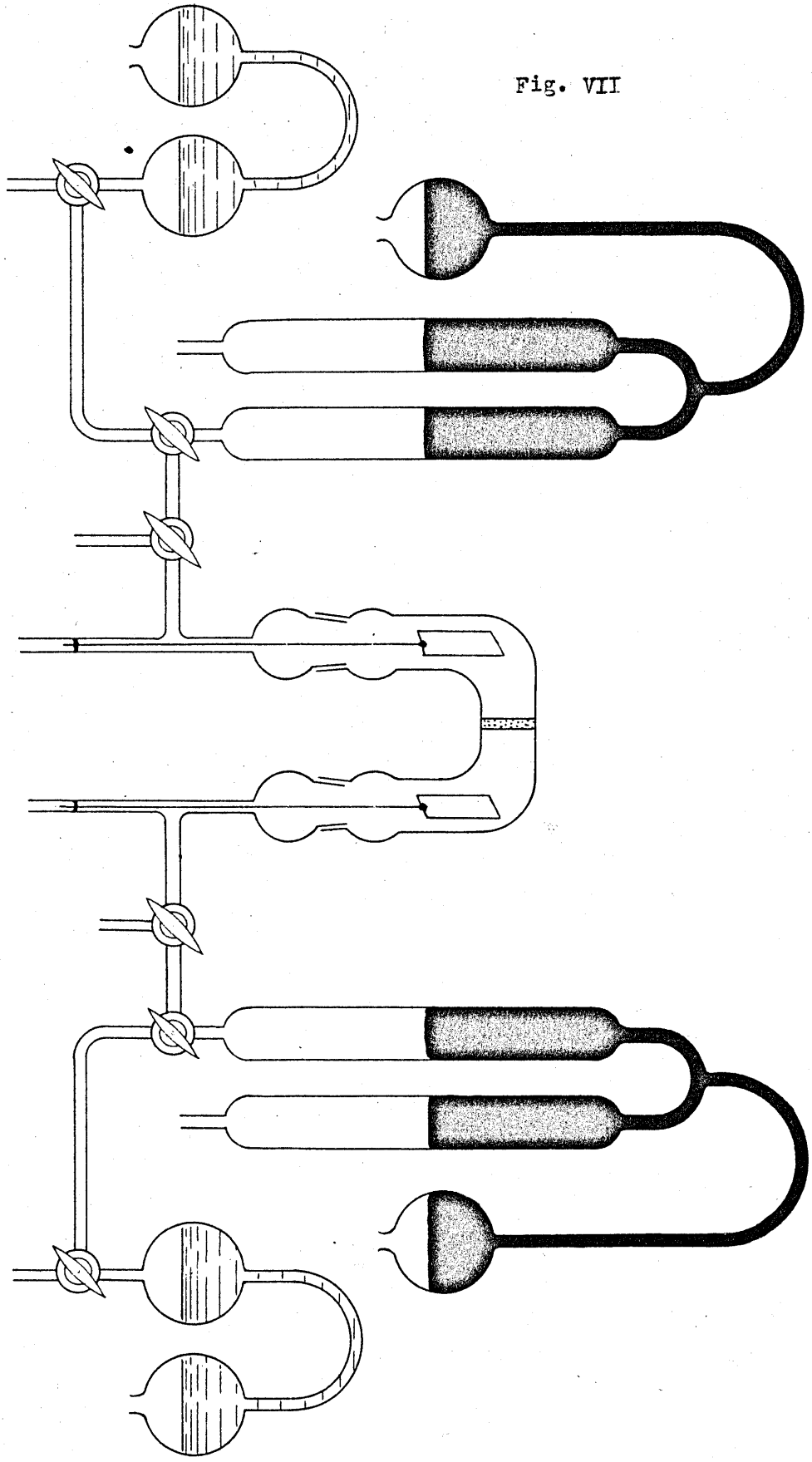
Experiment number 19 of Table V was carried out in order to determine whether or not any of the gaseous products formed exhibited reducing power. All gases evolved during the electrolysis were passed through Tollens' reagent; no reduction was observed. After the termination of the electrolysis the evaporated ammonia, carrying with it any gases left in the cell or dissolved in the solvent, also was passed into the reagent. Again no reduction was observed.

Measurements of the gases formed as a result of the electrolyses of ammonium nitrate-bromide mixtures were carried out in the following manner. The determination of the amount of gas evolved during the electrolysis was made by the method described in the "Procedures" section. The determination of the amount of gas dissolved in the ammonia, or the gas evolved only after the ammonia was boiled off, was made by absorbing the evolved ammonia in a sulfuric acid solution and collecting the insoluble gases. The amount of hydrogen in the gases evolved was determined by combustion analysis.

The results of the above gas measurements were as follows. When the concentration of electrolyte was low the amount of hydrogen evolved from the cathode compartment was less than that expected from normal cathodic hydrogen evolution. Tests for nitrite ion in the solid and dissolved products resulting from these electrolyses showed no more than trace amounts to be present. Similar electrolyses carried out in the small divided cell of Fig. VII gave evidence that nitrogen was evolved both from the anode and cathode compartments. Small amounts of hydrogen were observed to be evolved from the anode compartment.

The above results show that a competing reaction occurs at the cathode which does not consist in the reduction of nitrate to nitrite. The results also indicate that this competing reaction results in the formation of nitrogen.

Fig. VII



Nitrogen evolved in the anode compartment, and attributable to the reducing power of the lower valent aluminum found (rather than to anodic oxidation of ammonia), would be expected to stem from the reduction of the nitrate ion. A possible means of determining whether or not nitrate is so reduced is to find, by direct analysis, the amount of nitrate lost during the electrolysis.

The following method of analysis was used (17). The sample of nitrate was placed in a 250 cc. Erlenmeyer flask and 25-50 cc. of standardized 0.18 N ferrous ammonium sulfate were added (50% excess recommended), followed by 70 cc. of 12 N hydrochloric acid. Enough sodium carbonate was placed in the flask so that the evolved carbon dioxide excluded all air. The vessel was then immediately stoppered with a rubber cork having two outlets. One outlet was provided with a dropper containing 3 cc. of 1% ammonium molybdate solution as catalyst. The other opening contained a glass tube connected to a piece of Tygon tubing the other end of which was immersed in a saturated solution of sodium carbonate.

The solution in the flask was heated to boiling, and after two to three minutes the catalyst was added. The boiling was continued for ten minutes; then the flask was cooled, so that the sodium carbonate solution was drawn into the acid and carbon dioxide was evolved.

After the solution had cooled to room temperature, 35 cc. of 6 N ammonium acetate solution was added for every

50 cc. of solution to be titrated, and 5 cc. of 85% phosphoric acid were introduced. The solution was slowly titrated with standard 0.1 N potassium dichromate solution, six to eight drops of a saturated solution of diphenylamine sulfonate serving as an indicator.

The calculations were made upon the basis of the reduction of the nitrate ion by ferrous ion to NO according to the equation

$$3Fe^{++} + NO_3^- = 3Fe^{+++} + NO + 2O^=$$

Two trial analyses of pure ammonium nitrate gave results as follows:

Weight NH_4NO_3	No. of moles NH_4NO_3	No. of equivalents Fe utilized	Calculated no. of moles of NH_4NO_3	Percentage of NH_4NO_3 found in sample
grams				
0.0532	0.000666	0.001992	0.000663	99.6%
0.0793	0.000991	0.002965	0.000988	99.7%

Two experiments were carried out in the simple cell of 25 cc. capacity. In these experiments the amount of hydrogen evolved was determined by combustion analysis, and was found to be less than that expected from normal cathodic reduction of ammonium ion. In order that the results of the determinations of nitrate ion loss may be properly evaluated, some hypothesis must be made concerning the competing cathode reaction. Since, in other experiments similar to this, tests have shown little nitrite ion to be formed, it may be assumed

that the nitrate is reduced to nitrogen at the cathode as a competing reaction to the liberation of hydrogen. During these electrolyses, especially toward the end, the blue coloration characteristic of the liquid ammonia solution of aluminum was observed at the surface of the cathode. From this fact it seems that the primary competing reaction at the cathode is really the formation of the aluminum solution, the reduction of the nitrate to free nitrogen being a secondary reaction.

If we know the amount of hydrogen formed, the loss of nitrate ion, and the number of faradays of electricity used, and if our postulates concerning the natures of the cathode and anode reactions are correct, we should be able to calculate the apparent initial valence number.

If we assume that all of the nitrate lost is reduced to nitrogen, then the number of equivalents of reducing power accounted for is five times the number of moles of nitrate lost. This number of equivalents added to the number of equivalents of hydrogen formed must be equal to the total reduction occurring during the experiment; i.e., the number of equivalents of reduction at the cathode (the number of faradays of electricity) plus the number of equivalents of reducing power to be expected at the anode due to the presence of the lower valent aluminum formed.

The apparent initial valence number is thus calculated:

$$V_I = \frac{3 \times (\text{no. of faradays})}{(\text{equiv. of reduction})}$$

Or:

$$V_I = \frac{3 \times (\text{no. of faradays})}{5 \times (\text{no. of moles of } NO_3^- \text{ lost}) + (\text{no. of equiv. of } H_2)}$$

The data and results for these two experiments appear in Table VI. The significance of the column headings is as follows:

A. No. of gram atoms of aluminum dissolved at anode.

B. No. of faradays of electricity passed through the cell.

C. Apparent initial valence number calculated from A and B above.

D. No. of moles of nitrate ion reduced (from nitrate analysis and initial amount of this ion present).

E. No. of equivalents of hydrogen evolved from the cell (determined by combustion analysis).

F. Total reduction during the electrolysis (5D+E).

G. Apparent initial valence number as calculated from F and B.

The first two experiments, described in Table VI, were those in which the loss of nitrate was determined by the analysis using ferrous iron reduction. In the third experiment, the nitrate analysis was made by a less accurate method based on the measurement of the nitric oxide evolved upon the reduction of the nitrate by mercury. In this case, the gases evolved

TABLE VI

No.	A	B	C	D	E	F	G
(1)	0.001928	0.003783	1.75	0.000641	0.002513	0.005718	~~1.77~~ 1.98
(2)	0.00208	0.00446	2.15	0.000751	0.00256	0.00622	~~2.15~~ 2.12
(3)	0.002002	0.003593	~~1.80~~ 1.79	0.000773	0.001955	0.005820	~~1.83~~ 1.85

were not analyzed for hydrogen; thus, the figure appearing in column E was determined by subtracting the theoretical amount of free nitrogen from the total amount of gas.

The excellent agreement of the values of the apparent initial valence numbers as calculated by the two different methods (columns C and G) attests to the correctness of the assumptions. The results show also that no competing reaction, such as the oxidation of amide ion, occurs at the anode. This is in contrast to the results obtained in the case of the use of nitrates alone as electrolytes, in which case evidence of the oxidation of amide was obtained. This contrast suggests that the lower initial valence numbers obtained in the case of nitrate-halide mixtures may be explained in part by the absence, in the latter case, of any passivity of the anode; i.e., by the absence of any anode reaction other than the dissolution of aluminum.

If the above interpretation of the studies of the reduction of nitrate is correct, the apparent initial valence number should be calculable also from the amount of nitrogen evolved. This, however, would be a much less accurate method, since only a small volume of this gas is evolved, and its magnitude must be determined from the difference between the total volume of gas evolved and the volume of hydrogen as measured by combustion analysis.

An example of this type of calculation, from the data of experiment 29 of Table IV. This electrolysis was carried

out in the divided cell of fig. VII.

$$VI = \frac{3x(\text{no. of faradays of elect.})}{(\text{no. of moles of } N_2)x10+(\text{no. of equiv. of } H_2)}$$

No. of faradays of electricity---------- 0.004917
Vol. of nitrogen (cc.)----------10.7
No. of moles of nitrogen---------- 0.000478
Vol. of hydrogen (cc.)----------47.4
No. of equivalents of hydrogen---------- 0.00424

$$V_I = \frac{3x0.004917}{0.000478x10+0.00424} = 1.63$$

The initial mean valence number as calculated from the weight loss of the anode was 1.52.

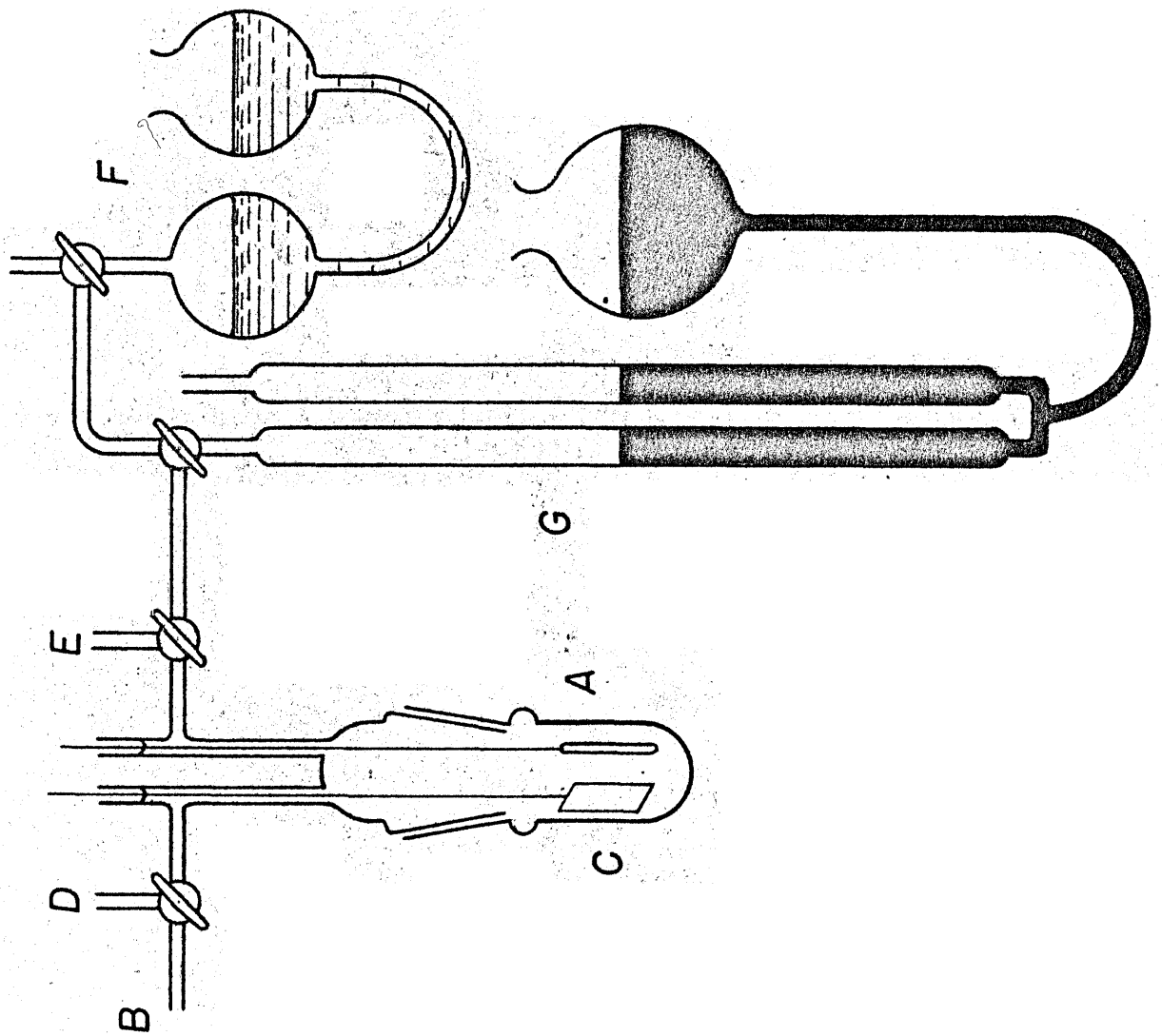
Even better results were obtained from data on an electrolysis carried out in the simple cell of Fig. VIII. The number of moles of nitrate ion present was less than the number of faradays passed. The data and results follow:

Mole % of bromide in electrolyte----------29.2%
No. of faradays of electricity---------- 0.002573
Vol. of nitrogen (cc.)---------- 3.7
No. of moles of nitrogen---------- 0.000165
No. of equivalents of nitrogen---------- 0.00165
Vol. of hydrogen (cc.)----------27.46
No. of equivalents of hydrogen---------- 0.00245
No. of eq. H_2+no. eq. N_2---------- 0.00410
Apparent initial valence number
from nitrogen data---------- 1.88
Apparent initial valence number
from loss in weight of anode---------- 1.90

Considering the possible errors in the determination of so small a volume of nitrogen, this agreement is very satisfactory.

During most of the electrolyses in which ammonium salts were used as electrolytes, a black finely divided substance

Fig. VIII



was formed at or near the cathode. The amount of this black material appeared to increase with increasing current density at the cathode and with decreasing concentration of the electrolyte, but no more than 12 mg. was obtained in any case. On analysis, it proved to be metallic platinum. It is not known whether this material resulted from mechanical disintegration of the cathode or from an electrode reaction. The greatest loss in weight of the platinum cathode amounted to only 0.00006 gram-atom of the element; hence, even if the process was electrolytic, it would correspond to no great interference with other cathode processes.

In experiment 30 of Table V, it was noted that some hydrogen was evolved while the ammonia was being boiled off. It is not known whether or not there is any connection between this gas evolution and the disintegration of the cathode. In this case the amount of delayed hydrogen amounted to about 0.00045 equivalent while the loss from the cathode was 0.000056 gram-atoms of platinum.

It was thought that the use of an aluminum cathode would eliminate any possible error resulting from the formation of the black product at the platinum electrode. Two electrolyses were carried out with aluminum cathodes, one in the simple cell of 60 cc. capacity, the other in the 60 cc. divided cell. The concentration of electrolyte in each case was high enough so that, if a platinum cathode had been used, nearly normal cathodic hydrogen evolution would have been obtained. In the

case of the simple cell the mole percentage of ammonium bromide in the electrolyte was 32.7, and in the divided cell electrolysis it was 27.2.

In the electrolysis in the simple cell, the total volume of gas evolved was 34% less than the volume of hydrogen expected at the cathode. Immediately after the electrolysis, and before the ammonia had been heated to above -78°, the solution was straw-colored. As soon as the ammonia was heated to a temperature near the boiling point, this color disappeared.

In the case of the divided cell, the products of the electrolysis were analyzed for nitrite ion. It was found that 0.00111 mole of this ion had been formed, while 0.00580 faradays had been used for the electrolysis. Evidently about 38% of the cathode reaction had consisted of the reduction of nitrate to nitrite. The occurrence of this competing reaction might be accounted for as resulting from a high hydrogen overvoltage of this type of anode. In this case also a yellow color was imparted to the solution; this color disappeared at higher temperatures.

In each of the above electrolyses the aluminum cathode was weighed before and after the experiment, and showed no loss in weight. The apparent initial mean valence numbers obtained in both cases were normal.

Intermittent Electrolysis

An objection that has been raised to the hypothesis that the aluminum enters the solution from the anode with a charge of less than +3 is that the anode might be non-electrolytically corroded. Since it has been shown that aluminum is not appreciably attacked on mere immersion in the solution used, this concept of non-electrolytic corrosion rests on the assumption that the anode is in some manner activated by the electrolytic process, and thus becomes able to react with the electrolyte.

The rectifier which had been used for the direct current source during this work was of the full-wave type, utilizing two mercury vapor tubes. When the cap of one tube was removed, the instrument became a rectifier of the half-wave type, giving an intermittent direct current; i.e., current flowed for periods of 1/120th second, separated by 1/120th second intervals of no current. If the electrode were "activated" by the electrolysis and if the "non-electrolytic corrosion" were to continue even for a short interval after the current is shut off, the apparent initial valence numbers obtained by the use of this modified rectifier should be less than those obtained with the use of a full-wave rectifier. Electrolyses numbers 14 and 15 of Table V were carried out with the use of a half-wave rectifier; it may be seen that the results were essentially the same as when the full-wave current source was used. Hence any "non-electrolytic" corrosion must take

place, if at all, only simultaneously with the passage of current; under these conditions, it is difficult to see how it could be distinguished, either theoretically or experimentally, from electrolytic oxidation.

Effect of Oxygen

An experiment was carried out in the large divided cell of Fig. II, with ammonium bromide as electrolyte, to determine what effect, if any, the presence in the cell of oxygen gas might have upon the apparent initial valence number. During the course of the electrolysis oxygen was bubbled through the ammonia solution in each compartment of the cell. A current of 0.03 ampere was used, giving an anodic current density of 0.003 amp./cm.^{2} The apparent initial valence number obtained was 2.96. Thus the oxygen had no obvious effect upon the apparent valence number obtained. The products of the electrolysis, however, exhibited some oxidizing power, liberating iodine from an acidic KI solution.

Use of Complexing Agents

A few experiments were carried out in which various complexing agents were added to the electrolyte in order to determine their effect upon the apparent initial valence numbers.

An electrolysis was carried out in the large simple cell of Fig. I, at the boiling point of the solution, with

zinc nitrate as electrolyte and pyridine as complexing agent. No appreciable change of valence number was observed; the value of 2.87 obtained is much the same as those found under similar conditions without the presence of pyridine. Similar experiments with ethylenediamine also showed no change of valence number.

Aluminum triiodide was tried as an electrolyte in the presence of α,α'-dipyridyl in the large simple cell of Fig. I. Following are the data and results:

Volume of ammonia (cc.)---60 Weight loss of anode (g.)-0.0553
Weight of AlI_3 (g.)-------1.5 No. of faradays----------0.00605
Weight of α,α'-dipyridyl (g.)-1
Apparent initial valence number----------2.96

Although there appears to be no change of valence number from the expected value, some qualitative observations made during this electrolysis were of considerable interest. After about 15 minutes of operation with a current of about 0.15 ampere, the blue color characteristic of the solution of aluminum in liquid ammonia was observed. As the electrolysis continued, a very intensely colored solution was formed. This solution retained its color when filtered off, and a light pink solid remained in the cell. When the liquid ammonia was evaporated from the colored solution, a brown residue was left. The solution attained a red color when evaporation was just short of complete.

Dissolution of sodium metal in a liquid ammonia solution containing α,α'-dipyridyl gave, at first, a deep blue solution

which soon changed to a deep red. Evaporation of the solution left a small amount of a yellowish white substance, which was not identified.

Electrolysis of a zinc chloride solution containing α,α'-dipyridyl between a zinc anode and a platinum cathode gave a similar blue solution. Some red material was deposited at the bottom of the cell.

Since these very interesting phenomena were not directly related to our problem, they were not studied further. The following question remains unanswered: Is this blue solution which is formed in the electrolysis of aluminum or zinc salts related directly to the "ammoniated electron solution" of alkali metals, or is the color that of some reduction product of the α,α'-dipyridyl?

SUMMARY AND CONCLUSIONS

When the following substances were used as electrolytes, in the anodic oxidation of aluminum in liquid ammonia, apparent initial valence numbers very near to 3 were obtained:

AlI_3 $CuBr_2$ NH_4Br $NaSCN$ KIO_3 Aluminum acetylacetonate

The following substances, when used as electrolytes, caused the anode to become passive towards the dissolution of aluminum:

$NaNO_2$ $KMnO_4$ NH_4OOCCH_3 Ammonium salicylate

Apparent initial valence numbers of less than 3 have sometimes been obtained. These low valence numbers were found, however, only when certain specific electrolytes were used. These electrolytes were:

$Al(NO_3)_3$ $NaNO_3$ NH_4NO_3 $Cu(NO_3)_2$ $Zn(NO_3)_2$

The apparent initial valence numbers obtained by the use of these electrolytes were in the neighborhood of 2.7.

Considerably lower apparent initial valence numbers were obtained by the use of mixtures of electrolytes. These mixtures were:

(1) $NaNO_3$-----NaBr

(2) $NaNO_3$-----NaCl

(3) NH_4NO_3----NH_4Br

(4) $Cu(NO_3)_2$--$CuBr_2$

(5) $AgNO_3$-----AgBr

The valence numbers obtained with these mixtures did not depend upon the nature of the cation, but showed regular dependence upon the ratio of the quantities of the two substances in the solute. With the use of nitrate-bromide mixtures, initial valence numbers as low as 1.42 were obtained. The minimum valence numbers occurred when the electolyte contained about 1 mole of bromide for each 2 moles of nitrate. In the case of the nitrate-chloride, a minimum initial valence number of 1.62 was obtained when the electrolyte contained about 1 mole of chloride to 1 of nitrate.

Intermediate values for the apparent initial valence number were obtained when the following mixtures were used:

(1) $NaNO_2$----NaBr

(2) $NaNO_3$----NaCN

(3) $KClO_3$----NaBr

In the first two cases, in which there was evidence of passivity of the anode, there appeared to be no regular dependence of the initial valence number upon the relative proportions of the substances. Since only one experiment was carried out with the third mixture, the effect of changing the relative proportions of the two substances is unknown.

In the case of the nitrate-bromide mixtures, no lower valent aluminum could be isolated. We have shown that such aluminum is oxidized by the nitrate ion to the tripositive state, the nitrate being reduced to free nitrogen. There was

evidence also of the reduction of ammonium ion to give hydrogen. The apparent initial valence number appeared to show no dependence upon the current density at the anode and also, as long as conditions were such that the nature of the electrolyte was not altered, there appeared to be no effect of change of concentration of the solute. Evidence was obtained that the formation of lower valence states is favored by high temperatures.

In the case of the nitrite-bromide mixtures the lower valent aluminum appears to disproportionate, with the formation of free, highly active, aluminum and the tripositive ion.

Three tests were carried out for the purpose of detecting non-electrolytic corrosion. They are as follows: (1) Samples of aluminum were exposed to solutions which had given low mean valence numbers. In no case was any loss in weight of these samples noted. (2) Aluminum cathodes were used in electrolyses which gave low initial valence numbers. In no case did such a cathode lose weight. (3) Intermittent electrolyses were carried out in such a manner that spaced direct current pulses were applied to the cell. No departure from the expected initial valence numbers was noted.

With the use of nitrates, nitrate-bromide mixtures, or nitrate-chloride mixtures as electrolytes, no evidence was found of mechanical disintegration of the anode.

The specific part played by the nitrate ion in bringing about the occurrence of low apparent valence numbers is not

known. The reason for the fact that especially low apparent valence numbers are obtained with certain mixed electrolytes is unknown also.

The conclusions to be drawn from this work are as follows. Under certain conditions the anodic oxidation of an aluminum anode in liquid ammonia produces, initially, aluminum ions with a mean valence of less than 2. This lower valent aluminum either reacts with the electrolyte, being oxidized to the tripositive state, or it disproportionates with the formation of metallic aluminum and the tripositive ion. The lowest mean valence found corresponds to the formation of about three unipositive aluminum ions for each tripositive ion.

SUGGESTIONS FOR FUTURE INVESTIGATIONS

The studies carried out in this work have by no means covered completely the entire list of electrolytes that could be tested for their effect upon the apparent valence number. There may be some inorganic or organic electrolyte which would promote the formation of lower valence states, and which would also allow the isolation of lower valent aluminum compounds.

The effect of changing the ratio of the anions in chlorate-bromide mixtures was not determined. Such a study might reveal a relationship similar to that found for the nitrate-bromide mixture.

A study of the anodic oxidation of metals in the solvent ethylenediamine might prove interesting a trial electrolysis with ammonium bromide as an electrolyte in this solvent gave an apparent valence number for aluminum of 2.74.

Another interesting study would be the determination of the character of the intensely colored solution resulting from the presence of α,α' -dipyridyl during the electrolysis of aluminum or zinc halides.

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